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This document appeared in

Detlef Stolten, Thomas Grube (Eds.):
18th World Hydrogen Energy Conference 2010 - WHEC 2010
Parallel Sessions Book 4: Storage Systems / Policy Perspectives, Initiatives and Co-operations
Proceedings of the WHEC, May 16.-21. 2010, Essen
Schriften des Forschungszentrums Jülich / Energy & Environment, Vol. 78-4
Institute of Energy Research - Fuel Cells (IEF-3)
Forschungszentrum Jülich GmbH, Zentralbibliothek, Verlag, 2010
ISBN: 978-3-89336-654-5

Advantages of Organic Chemical Hydrides for Long-term Storage and Over-sea Transportation of Hydrogen

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Summary

Wind-power hydrogen is convertible into methylcyclohexane via catalytic hydrogenation of toluene and becomes storable for long term as well as transportable over sea. Catalytic dehydrogenation of methylcyclohexane would contribute to CO_2 reduction at energy-demand sites in industries, e.g., electric power, steel making, automobile, town-gas, etc.. Key technology in the present system lies on dehydrogenation catalysis, which involves endothermic hydrogen evolution.

It was elucidated for the first time that heating temperatures could be lowered down to 300-C and below, where adsorbed species were removed under vigorous boiling conditions, making it possible to accelerate the regeneration of active sites. A flow-type catalytic reactor, driven by low-quality heats, was discussed from the viewpoint of exergy analysis in contrast to liquefied hydrogen.

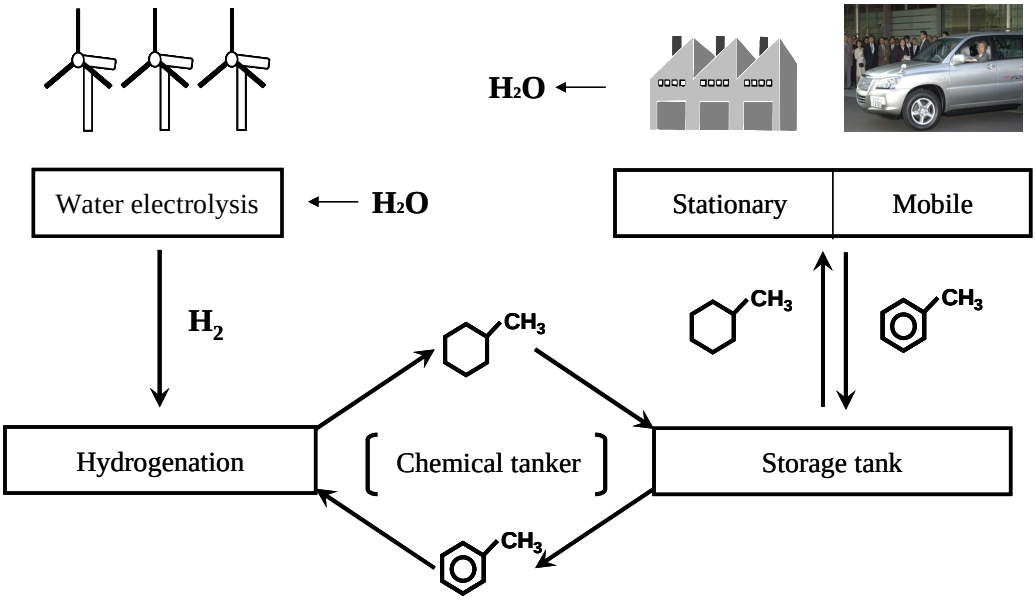


Figure 1: Storage and Transportation System for Hydrogen by Organic Chemical Hydride.

1 Introduction

The most important for hydrogen storage is to be safe in addition to be easy-to-handle. Organic chemical hydrides are hydrocarbons with moderate boiling points and volatilities (Table 1), the ranges of which belong to gasoline. A catalytic reaction couple of toluene hydrogenation and methylcyclohexane dehydrogenation makes it possible to store hydrogen at the levels of 6.16% in weight and 1.33 times larger than liquefied hydrogen in volume [1]. Among secondary energies, electricity is superior to others in many aspects, but is disadvantageous to transport over the sea in contrast to chemicals. A series of renewable-energy technologies, consisting of wind power, water electrolysis and hydrogenation catalysis, is particularly attractive, because organic chemical hydrides are storable for long term and can connect foreign industrial countries with emblessed wind-firm areas at any place in the world.

Hydrogen regeneration from organic chemical hydrides has a serious task, however, where the endothermic reaction heat is required at the energy-demand sites. By this reason, a certain kind of waste heats ought to be utilized at the temperatures as low as possible. Hydrogen storage with organic chemical hydrides will therefore be discussed with special emphasis of dehydrogenation catalysis in the present work.

2 How to Make and Carry Hydrogen at a Large Scale

Renewable energy is concentrated and stored as wind power on earth in the polar regions. From the North Pole, strong wind blows through the Behring Sea to the North Pacific, which brings the Aleutian Islands tremendous wind resource at annual average of ca. 10 m/s. Since a large-scaled windfirm as 50 GW is capable to be built there, wind hydrogen is now planned to convert it into organic chemical hydrides. Production of hydrogen from the windmill at Aleutians will amount to 3.8 million tons per year. Dutch Harber, a famous unfrozen fishery port in Alaska, had long been connected with Los Angeles and Yokohama, both being apart from ca. 5000 km. This area is assumed to be the center for the factories of water electrolysis and catalytic hydrogenation of toluene to yield methylcyclohexane.

$$\text{methylcyclohexane (MCH)} \rightleftharpoons \text{toluene (TOL)} + 3\,H_2 \qquad \Delta_r H\text{: } 67.5 \text{ kJ mol-}H_2^{-1}$$

Table 1: Molecular properties of organic chemical hydrides.

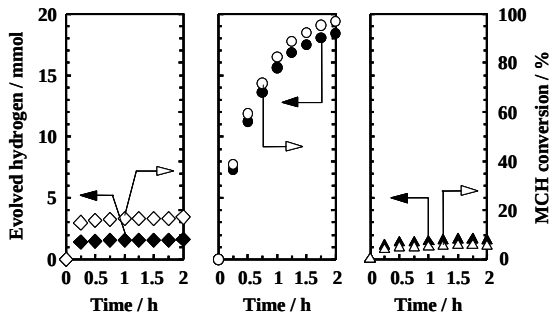
	bp/℃	mp/℃	vapor press. (25℃)/kPa	hydrogen content/wt%
MCH	101.1	-126.6	6.1	6.16
TOL	110.6	-95.0	2.9	

3 How to Regenerate Hydrogen from Organic Chemical Hydrides

Methylcyclohexane, imported to an industrial country and kept at the port storage tank, is transferred by lorry or pipe to hydrogen-demand sites, where the reaction heat of 67.5 kJ mol-H_2^{-1} is provided with waste heats from both economical and safety reasons. In this context, developments in low-temperature catalysis for dehydrogenation are strongly required.

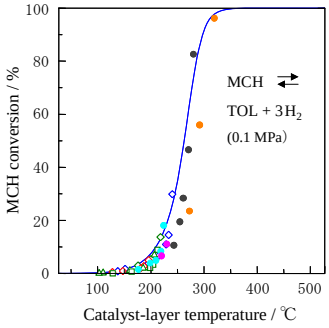
An appropriate wettedness, defined as the amount ratio of liquid MCH to carbon-supported catalyst, was found to take the essential role for dehydrogenation under boiling conditions. As shown in batch-type performances (Fig. 2) [2], subtle differences in wettedness were decisive in hydrogen evolution rates as well as 2 h-conversions. Equilibrium attainments were observed in flow-type reactors at the catalyst-layer temperatures in the range of 200~300-C (Fig. 3) [3]. The temperature gradient inside the catalyst layer and bubble evolution from the catalyst surface would couple vector-wise thermodynamically, by which the reverse path or toluene hydrogenation was prohibited irrespective of temperatures [4]. Preparation of nano-catalysts is essentially important [5].

In order to carry hydrogen with organic chemical hydride, a moderate thermal exergy is required for endothermic dehydrogenation, while the reverse process of toluene hydrogenation proceeds by removing the exothermic reaction heat. Total exergy loss for hydrogen storage is dramatically decreased, if compared to the extensive loss of mechanical exergy for hydrogen liquefaction.



Pt-Ir / C (5 wt-metal%, Pt / Ir = 4, 0.30 g), Heated at 210℃
MCH charged / ml (◆, ◇ : 0.4, ●, ○ : 0.8 , ▲, △ : 1.2)

Figure 2: Time courses of hydrogen evolution from methylcyclohexane in a batch-type catalytic reactor under boiling and refluxing conditions.



Pt / AC Cloth (3 ~ 5 cm ϕ & 10×20 cm^2, 5 wt%),
Fed at 0.3 ~ 3.5 ml-MCH min^{-1} without refluxing

Figure 3: Observed conversion from MCH in a flow-type catalytic reactor under boiling conditions.

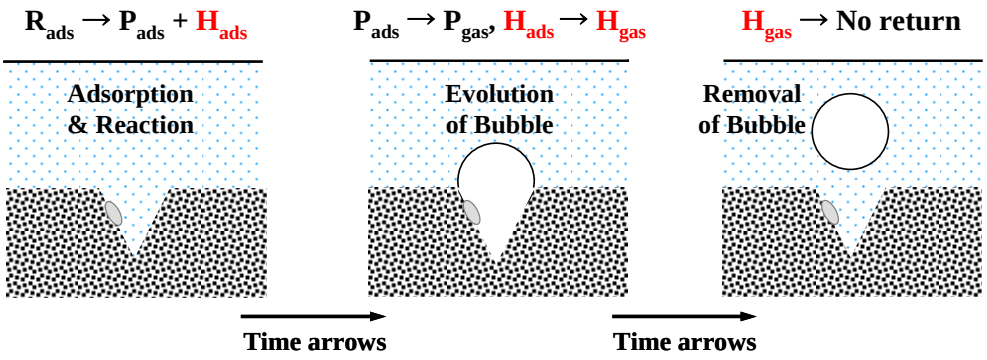


Figure 4: Contrariety from micro-reversibility principle in bubble evolution during dehydrogenation catalysis.

4 How to Utilize Hydrogen of Organic Chemical Hydride

Japan is surrounded and isolated by the sea from all kinds of energy resources. For example, American or Eurasian countries could choose pipe-line transportation of natural gas, whereas Japan had to start with LNG from the beginning. Either oil or coal had long been imported from abroad.

The present project of hydrogen storage and transportation as organic chemical hydride seems to open a new era on the following grounds.

1. Hydrogen is originated from the renewable energy of North-Polar wind.
2. Annual speed average (> 10 m/s) generates electricity (50 GW) at the Aleutian Islands.
3. Electrolysis hydrogen (3.8 million ton-H_2/y) is carried as organics in oil tankers.
4. Industrial waste heats (< 300-C) are available for endothermic hydrogen regeneration.

Renewable hydrogen, brought into Japan extensively, would contribute to CO_2 reduction (15 million ton-CO_2/y in calorie equivalent to H_2) through various industrial and domestic fields.

- Electric power: Hydrogen fuel to Molten Carbonate and Solid Oxide Fuel Cells.
- Steel making: Coke reduction in blast furnace processes by direct injection and ore prereduction.
- Town gas: Combustion-heat adjustment by hydrogen addition within the range of legal regulation.
- Domestic cogeneration: H_2 supply at Polymer Electrolyte Fuel Cell with use of its waste heats.
- Automobile: H_2 station for Fuel Cell Vehicles and on-board use for Internal Combustion Engines.

5 Conclusions

Both prolonged storage and distant transportation are superior properties of hydrogen to electricity as secondary energies. Organic chemical hydride has not only peculiar advantages to be safe and easy-to-handle, but also to be responsible to utilize waste heats for industrial and domestic consumers at the moments of hydrogen regeneration. Developments of large-scaled renewable energies will open a new paradigm of hydrogen economy.

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